

SEVENTH QUARTERLY REPORT
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COVERING
ALKALINE BATTERY SEPARATOR STUDY
December 29, 1963 to March 28, 1964
Contract NAS-5-2860

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N O T I C E

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I. INTRODUCTION

This is the Seventh Quarterly Report, covering work done during the period December 29, 1963 through March 28, 1964 on Contract NAS-5-2860.

II. WORK ACCOMPLISHED DURING THE REPORTING PERIOD

A. Ion-Exchange Membranes

The presently used ion exchange membranes battery separators are characterized by a high degree of chemical inertness. Their reactivity is low with all components of alkaline batteries. The membranes which have been synthesized under this contract contain monomers chosen for their stability to oxidation, and the reliability of this estimate is seen by comparing their resistance to attack by alkaline permanganate and to dissolved silver oxide. Cellophane and cellulose in general are marked in our screening tests, and also by a long history of battery testing, by ease of oxidation and degradative hydrolysis by the electrolyte. Cellulosic separators react quantitatively with small amounts of silver oxide dissolved in alkali. Our attempts to measure diffusion of the silver complex ion through cellophane and the various sausage casings was frustrated by this reactivity. Tagged silver in complex ion form disappeared from the "hot" side of a diffusion cell (the two halves of which were separated by a cellulosic diaphragm), but did not reappear on the other side of the diaphragm. Tagged silver was found to have concentrated in the separator. Those separators which were designed to be oxidation resistant did not react or had a limited capacity to react with oxidants and allowed diffusion of radioactive silver to occur. Quite probably, the reactivity of cellophane combined with its physical characteristics explains its unique functioning in silver zinc and silver-cadmium batteries.

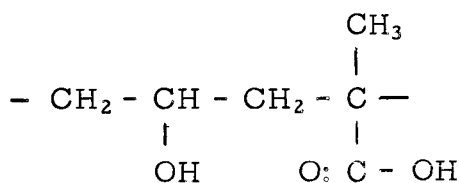
The instability of cellulose to hydrolysis, and the effect of dissolved and gaseous oxygen on the rate of hydrolysis is also a serious limitation to long lived batteries.

A combination of polyvinyl alcohol, which has been shown to undergo oxidative degradation in silver-zinc batteries, and polymethacrylic acid, which has been shown to be highly inert, should provide a separator system in which conductivity, absorption and chemical reactivity can all be varied. Hydrolytic stability should not be a problem in this series. To this end, ion exchange separators were made by polymerizing various monomers within the pores of

microporous polyethylene. The general procedure was to soak these polyethylene sheets in the monomer and catalyst mixture. After soaking, the wetted sheet was placed between two cellophane films, then sandwiched between glass plates. The assembly was placed in an oven and uniform pressure applied for a determined time interval at a suitable temperature. The first membrane made was a copolymer of vinyl acetate and methacrylic acid. The methacrylic acid was used to provide ionogenic groups necessary for good conductivity. Since monomeric vinyl alcohol is nonexistent, quickly rearranging to acetaldehyde, vinyl acetate monomer was polymerized to polyvinyl acetate, and converted by alcoholysis to polyvinyl alcohol. The first mix contained:

80 pts vinyl acetate
 20 pts methacrylic acid
 4 pts divinyl benzene (cross-linking agent)
 3 pts benzoyl peroxide (catalyst)

The copolymer would have the following repeating unit:



Membranes (.004" dry thickness) made from this mix had an electrical resistance of .039 Ω for an in² in 40% KOH. Since this resistance is moderately high, the ratio of vinyl acetate to methacrylic acid was adjusted to 50 parts vinyl acetate to 50 parts methacrylic acid. By increasing the percentage of methacrylic acid, more carboxylic groups capable of ion-exchange are introduced into the polymer. This reduced the electrical resistance to .025 Ω for an in². Again the monomer ratio was changed to 20 parts vinyl acetate to 80 parts methacrylic acid, the cross-linking percentage and catalyst concentration remaining constant. The electrical resistance was now measured at .017 Ω for an in² in 40% KOH. Oxidation tests in alkaline permanganate were run on these membranes. As the proportion of methacrylic acid was increased, the weight loss during oxidation decreased. The 50/50 membrane lost 40% while the membrane containing 80 parts methacrylic acid lost 30%. Another phase of this work was the effect produced by increased percentages of divinyl benzene, the cross-linking agent. As the percentage of divinyl benzene was increased, in all cases the electrical resistance increased. Cross-linking reduces membrane expansion and electrolyte absorption and so creates a higher electrical resistance. The following

table shows the change in electrical resistance caused by increasing the amount of divinyl benzene in different monomer compositions.

TABLE I

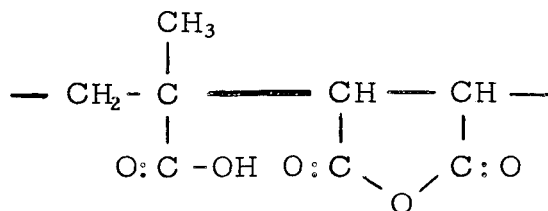
Electrical Resistance (Ω for an in.²) in 40% KOH

<u>Monomer Ratio</u>	<u>Divinyl Benzene 3.9%</u>	<u>9.1%</u>	<u>13%</u>
1 Vinyl acetate 4 Methacrylic acid	.017	.037	----
1 Vinyl acetate 1 Methacrylic acid	.025	.063	.075
4 Vinyl acetate 1 Methacrylic acid	.039	.087	.095

Since several of these membranes exhibit low electrical resistance, and improved resistance to oxidation, their ability to stop silver will be tested. Another ion-exchange membrane was made by copolymerizing maleic anhydride and methacrylic acid. These membranes were made in the same manner as the vinyl acetate membranes with the exception that a small amount of dimethyl formamide was used to dissolve the maleic anhydride. Maleic anhydride will not normally homopolymerize, so that varying the monomer ratio will not affect the composition of the resultant copolymer. The monomer ratio used was 1 to 1. The composition of the mix was:

60 pts maleic anhydride
 25 pts dimethyl formamide (solvent)
 51 pts methacrylic acid
 6 pts divinyl benzene (cross-linking agent)
 2 pts benzoyl peroxide (catalyst)

The copolymer would have the following repeating unit:



When the copolymer is subjected to hydrolysis, the anhydride ring opens, theoretically forming three successive carboxyl groups capable of specific chelate effects. The electrical resistance in 40% KOH measured .020 Ω for an in². The concentration of cross-linking agent was increased to 9.0%, and then to 13.0% to determine the effect on oxidation and electrical resistance. The following table shows the results of these experiments.

TABLE II

% Divinyl Benzene	Electrical Resistance Ω for an in ²	%wt loss in KMnO ₄
5.2	.020	33
9.0	.042	25
13.0	.079	23

As the degree of crosslinking is increased the resistance is also increased, but the percent weight loss during oxidation is decreased. By varying the degree of crosslinking, it is possible to produce properties that approach desired requirements. The effect of crosslinking on electrical resistance in both sets of ion-exchange membranes is shown in the following table.

TABLE III

Electrical Resistance (Ω for an in²) in 40% KOH

Percent cross-linking	Methacrylic acid Vinyl acetate (1:1)	Methacrylic acid Maleic anhydride (1:1)
9.0	.063	.042
13.0	.075	.079

The methacrylic acid and vinyl alcohol copolymer membranes and the maleic anhydride-methacrylic acid copolymer membranes will undergo testing to determine their suitability as battery separators.

An ion exchange membrane, prepared by copolymerizing methacrylic acid with i-propyl acrylamide within the pores of microporous polyethylene has been mentioned in our Sixth Quarterly Report (p 6); its testing has been completed. The electrolyte absorption and retention are remarkably high, with values closely approaching those of cellophane (see Table IV, sample No. 32).

The electrical resistivity is also very close to - in fact, slightly below - that of cellophane (see Table VI). Furthermore, the swelling values of this membrane are fairly low. In view of these favorable results, this material will be examined more closely.

Permion 1000, a carboxyl modified Teflon membrane made commercially by Radiation Applications Inc., was found to be dimensionally very stable but its electrolyte absorption and especially its electrolyte retention were low. Its specific resistivity was about three times that of cellophane. It is inert to silver oxides and no barrier to silver diffusion, as pointed out in our preceding report (pp 4-5).

B. Urethane Films

In the Fifth Quarterly Report, cellophane was coated with liquid urethane polymer to improve the oxidation resistance of the film. The oxidation resistance showed some improvement, but the electrical resistance remained high (6.5Ω for an in^2). Since liquid urethane polymers can be cured to strong, rubbery solids, the possibility of making an unsupported urethane film, filled with ion-exchange resin to improve conductivity, was investigated.

Adiprene "L" (Dupont) is a liquid urethane elastomer containing 4% isocyanate groups by weight. The elastomer is transformed from a liquid to a solid material by the reaction of the isocyanate group with polyamine compounds. The polyamine compound in this case was DuPont's MOCA, 4, 4' - methylene - bis - (2 - chloroaniline). The MOCA was dissolved in dimethyl formamide and XE-97, a polycarboxylic acid ion-exchange resin (Rohm & Haas Co.), was added. Then a corresponding amount of Adiprene "L" was stirred in. More dimethyl formamide was added to reduce the viscosity sufficiently to allow casting. Films were cast on silicone paper, and cured at 100°C for three hours. Different ratios of XE-97 to Adiprene "L" were used and the following resistance measurements were taken in 40% KOH. The swollen thickness of the films was .006 inches.

<u>Ratio</u>	<u>Resistance (Ω for an in^2)</u>
1 XE-97 5 "L"	4.36
1 XE-97 2 "L"	0.10
1 XE-97 1 "L"	0.029

If the ratio of the XE-97 to the Adiprene "L" is increased to 2 to 1, the film loses its resilience and cracks during cure. The 1 to 1 film, which had a resistance of $.029 \Omega$ for an in^2 , lost 28% by weight during permanganate oxidation. Swelling data and alkali resistance remain to be measured.

III. Cellophane Modifications

1. Treatment with Toluene Diisocyanate (TDI)

Continuing the investigation of the diisocyanate treatment of cellophane, we found that a high humidity atmosphere is essential to complete the reaction. When cellophane is immersed in a dilute solution of the diisocyanate and then dried immediately in an oven, the cellophane remains clear and becomes brittle, it is covered with a coating which adheres loosely and peels off on prolonged soaking in KOH. If, however, the TDI treated sample is exposed to a humid atmosphere, before any substantial amounts of the solvent can evaporate, the cellophane becomes opaque and remains flexible. Very little opacity develops at low humidities even if catalysts (methyl morpholine, di-n-butyltin diacetate) are added to the TDI solution.

The choice of the solvent proved also to have an important influence on the effectiveness of the treatment. When the diisocyanate was dissolved in ethyl acetate, little if any reaction occurred, even in a high humidity atmosphere. At first, it was thought that the low mutual solubility of the solvent with water was responsible for the unsatisfactory results. Acetone was, therefore, tried as the solvent for the diisocyanate; however, the result was no better. It appears that low boiling solvents must be avoided because they evaporate too fast to permit penetration of the water vapor into the diisocyanate layer. Dimethyl formamide (b.p. $152-154^\circ\text{C}$) has so far proved the best solvent for this purpose.

In preparing more samples, it was found that light deposits are preferable to heavier ones. Heavier coatings have a tendency to peel off and the electrical resistivity is appreciably increased by heavy deposits. The procedure described in the Fifth Quarterly Report (p 7) was therefore amended, as follows:

1. The preliminary drying was found to be unnecessary if the moisture content of the cellophane was not more than 5 - 6%.
2. The cellophane was immersed in a 5% diisocyanate solution in DMF (reduced from the original 10%).

3. The impregnated samples were quickly transferred to a high humidity oven, maintained at approximately 38°C and 90 - 100% RH. Two minutes under these conditions were sufficient to complete the reaction.

Electrical resistance values of treated samples were measured after 24 hours immersion in 31% KOH:

Sample	Observed Value R _o (ohms)	Resistance R ₁ (ohms - sq in.)	Spec. resistivity (ohms - cm)
a	.105	.016	12.6
b	.212	.032	25.4
c	.105	.016	12.6
Average	.141	.021	16.9
Blank	.062	.009	8.45

No measureable differences were found in thickness, either before or after soaking in KOH. Variations in degree of opaqueness were observed on the dry samples. The differences in resistivity appear, therefore, to be due to variable resin pick-ups. This observation points to the importance of closely controlling the amount of pick-up. Efforts to improve this control are continuing.

The cellophane used in these experiments was the glycerine-free product which is generally used in batteries. Samples of the more common, glycerine containing cellophane were also treated with TDI. It was hoped that the glycerine would take part in the isocyanate reaction and thereby contribute to the strengthening of the structure. The glycerine content in untreated and TDI treated cellophane PUD 600 was determined by water extraction, followed by cerate titration, with the following results:

Untreated	15.1% glycerol
TDI treated	11.6% glycerol

These results indicate that the TDI has indeed reacted with some of the glycerol but too much of the glycerol remains unreacted for use of the modified cellophane in a battery.

Cell tests with TDI treated cellophane (glycerol-free) have been initiated to obtain some preliminary information on the effects of the treatment on battery operation.

2. Gelatinized Cellophane

It is a generally accepted theory that the electrolyte permeability of cellophane and hence its low electrical resistivity are due to its porous structure. On the other hand, at least some of the pores are large enough to allow the passage not only of electrolyte but also of dissolved zinc ions. It seemed therefore desirable to reduce the permeability to larger ions without, however, impeding the transport of electrolyte through the membrane.

A somewhat similar problem was found to exist in the field of water desalination. A report from the Monsanto Boston Laboratories to the office of Saline Water, U. S. Department of the Interior (1) states that cellophane was unsuited as a membrane for desalination by the reverse osmotic process; although high water transmissions were obtained, the complete lack of salt rejection prevented its use. However, by treating cellophane with various salt solutions (ZnCl_2 , $\text{Al}_2(\text{SO}_4)_3$, LiClO_4), Monsanto succeeded in gelatinizing the surface of the cellophane, i.e. in closing the micropores at the surface. As a result, high degrees of salt rejection were obtained while maintaining the good water transmission.

We tried to apply this principle to the preparation of perm-selective cellophane. Of the three salts mentioned in the Monsanto report, only ZnCl_2 and $\text{Al}_2(\text{SO}_4)_3$ were used; lithium perchlorate was eliminated because of the danger inherent in the oxidative capacity of any residual perchlorate.

Samples of cellophane PUDO-300 were soaked one hour in a 20% solution of $\text{Al}_2(\text{SO}_4)_3$, washed and dried. The treated cellophane proved very brittle. After a few hours soaking in 31% KOH it disintegrated. The silver reaction rate of the treated sample was determined (see below) but other tests were omitted because it was obvious that this material could not be used as a separator material. The sample which had been treated with zinc chloride appeared far more promising. Cellophane PUDO-300 was soaked in a 20% ZnCl_2 solution (1 hour at room temperature). After washing and drying, the film was somewhat wrinkled but it had retained its flexibility. Tables VII, VIII and IX show the effect of prolonged immersion of the ZnCl_2 treated film (Sample No. 29), with the corresponding values for untreated cellophane (Sample No. 1). It is quite obvious that the treatment has sharply reduced the degree of swelling. Electrolyte absorption and retention values are reduced by the treatment but they remain fairly high (see Table IV). The wettability has remained virtually unaffected by the treatment, as demonstrated by the electrical resistance values after different soaking times (Table V).

The electrical resistivity is, if anything, slightly improved by the treatment (see Table VI). It appears therefore that the ZnCl_2 treatment has had no adverse effect on the electrolyte permeability of the cellophane.

The question remains whether the treatment has resulted in a reduction of the cellophane's permeability to zinc ions. We have started a systematic study of zinc dendrite growth, details of which are recorded elsewhere in this report. It is our intention to include the ZnCl_2 treated cellophane in that investigation to find out whether the treatment has indeed produced the desired result.

3. Treatment with Antioxidants

To complete the work described in the Sixth Quarterly Report, hydroquinone treated cellophane was subjected to the usual screening tests. The results, shown in the appended tables (IV through IX) indicate that the treatment has no marked effect on either the mechanical or the electrical properties of cellophane.

4. Silver Treated Cellophane

Two samples of silver treated cellophane, C-19-300 and C-19-600, were received from NASA - Goddard and were subjected to our screening tests. The results are listed in the appended tables IV through IX. They are in good agreement with the values for the corresponding untreated cellophanes (compare Nos. 31 with 1 and 32 with 2). Only the swelling values were generally substantially lower for the Ag treated samples than for the untreated samples.

IV. Dip Coating

Wrapping of electrodes with films which tend to break or crack often presents a problem; small cracks may go unnoticed but will quickly cause shorting in a battery. Forming permanently attached separator envelopes on the electrodes appeared to offer an attractive possibility for avoiding this danger. To form such membranes, it is only necessary to dip an electrode in a film forming material in a liquid form, e.g. a solution, dispersion or emulsion, and convert it into a solid membrane.

A carboxy modified latex was chosen because the carboxyl group makes it possible to utilize cross-linking through these groups in place of, or in addition to, the conventional sulfur cure. Vulcanization can be effected at lower

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temperatures and a fully cured vulcanizate should have improved oxidation resistance because of the higher crosslink density.

Good-rite 2570 x 5, a carboxylated butadiene-styrene copolymer latex of 40.9% solids content, made by B. F. Goodrich, was used. Sulfur, zinc oxide and accelerators were added to cure the polymer. A typical formulation follows:

	% Solids	Dry	Wet
Good-rite Latex 2570 x 5	40.9	100	244.5 g
Zinc oxide	59.3	5	8.4 g
Sulfur	66.7	2	3.0 g
Setsit # 9 (acceler.)	50	2	4.0 g
Antifoam B	35	<u>0.44</u>	<u>1.25 g</u>
		109.44	261.25

Zinc plates were first dipped in a coagulant bath (a solution of calcium nitrate in methanol), air-dried and then immersed in the compounded latex; after 3 minutes, they were withdrawn from the bath at a controlled rate (7.5 in. per minute) and dipped immediately, without prior drying, in hot but not boiling water. The purpose of this procedure was to obtain the required porosity by preventing the escape of the contained water from the uncured film. The cure was complete after 2 hours at 95° to 98°C. Adhesion of the films to the plate was poor and the films tended to split along the edges. This condition was improved by preheating the dipped film for 15 to 30 minutes in water at 55°C before raising the water temperature to 95°C. However, it became clear that the porosity was far too low when the electrical resistance, after 24 hours in 40% KOH, was measured; the lowest value was 73.5 ohms - sq in. Attempts to increase the porosity by dilution of the latex failed because the resulting films were too weak and cracked, even when the viscosity of the dipping bath was raised by the addition of thickeners (Alcogum N-10, Carbopol 941). Nor did substitution of an inherently stronger polymer - neoprene (in the form of neoprene latex No. 571) - for 25% of the Good-rite latex help; the cure time was lengthened without adequate strengthening of the film.

Since it had become obvious that water retention before cure could not be relied on to produce the required porosity, other means were tried.

a) Starch: A latex mix of the above mentioned composition was diluted by the addition of 100 ml water. 200 g of a 50% aqueous dispersion of corn starch were added. The plates were dipped, dried and the deposits cured. The cured films were leached two hours with hot dilute HCl but the electrical resistance was extremely high (2890 ohms - sq in.). Apparently the starch which had been deposited from the dispersion in latex could not be removed by the usual treatment with HCl because the particles were encapsulated by a film of elastomer.

b) Calcium carbonate: The starch was replaced by an aqueous dispersion of Lesamite (a fine particle size CaCO_3). Removal of the CaCO_3 from the cured film was attempted. The expected CO_2 evolution did occur momentarily but stopped within a few seconds - apparently again because of encapsulation of the filler particles by the elastomer. Addition of bromine water to the hydrochloric acid produced a sustained reaction but it resulted in rapid degradation of the rubber.

c) Colloidal Silica: DuPont's Ludox HS, containing 30% SiO_2 was added to the above latex compound (stabilized with 2 g morpholine), at a ratio of 30 parts SiO_2 per 100 parts elastomer. Stability troubles were encountered and the viscosity rose gradually. The mixture was not suited for dipping. Smooth films could be prepared by spreading, drying and curing (10 min at 140°C); the films were wrapped around zinc plates and tested in a cell; current passed through initially but dropped off rapidly. The explanation was found in the precipitation of the SiO_2 by the KOH, presumably in the form of non-hydrated silica gel.

d) Sugar: The latex compound tolerated the addition of substantial amounts of sugar but the sugar did not co-precipitate with the elastomer and a non-porous film resulted.

Further work with the dipping process was abandoned as holding no promise of success.

V. Growth of Zinc Dendrites

An investigation of the growth rate of zinc dendrites was initiated. The primary purpose of this study is to find means for measuring the ability of various separator materials to resist penetration by the growing dendrite. Once the method

has been established it might also become possible to develop modified materials with improved dendrite resistance.

A search of the literature has produced little information on the subject. Higgins, (2) in a study sponsored by a division of this company, has investigated the growth rate of zinc dendrites as a function of electrode composition, of zinc solubility in the electrolyte, of various electrolyte additives, and of current density; but his work did not include the effects of dendrites on various membrane materials. A Soviet publication, by T. A. Kryukova (3), deals specifically with the effects of dendrites on separator materials. Mme. Kryukova used both unmodified and modified poly (vinyl alcohol) and cellulosic membranes and reports striking improvements for her modified materials, especially for modified, regenerated cellulose. However, she does not indicate the nature of this modification (beyond the terse statement that "solutions" were used). It will therefore be necessary to study first the effects of dendrites on existing materials and examine a possibly quite broad range of modifications in a second phase.

The cell used in our investigation is shown in Photographs 1, 2 and 3. The container is machined from Plexiglass; its overall dimensions are: height $2\frac{1}{2}$ in., length $2\frac{3}{4}$ in., width $\frac{15}{16}$ in. The negative electrode is formed by a zinc rod, $\frac{1}{2}$ in. diameter, fitted in one wall of the cell. The positive electrode is an expanded zinc grid (50% porosity); it is positioned in a cut-out of the opposite cell wall. Between the two electrodes is a Plexiglass plate, $\frac{1}{4}$ in. thick, with a round collimator hole, $\frac{1}{2}$ in. diameter, in the center. Its purpose is to ensure parallel paths for the current.

In assembling the cell, the separator under test is placed next to the negative plate. A flat platinum wire gauze, approximately 0.005 in. thick 1 by 1 in., with a platinum lead wire is placed against the separator; it serves as a reference electrode. A suitably cut-out Teflon sheet, 0.010 in. thick, is used as a spacer to protect the platinum gauze and the separator when the cell is clamped together.

The separator material to be tested is cut to the outside dimensions of the cell ($2\frac{1}{2}$ by $2\frac{3}{4}$ in.) and small squares (approximately $\frac{3}{8}$ by $\frac{3}{8}$ in.) are then cut out to provide room for the clamping screws; the separators are soaked 24 hours in the electrolyte before being tested.

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The electrolyte is made by dissolving 100 g KOH pellets (86.6% KOH content) and 8 g ZnO in 100 g water. The assembled cell, with one layer of the separator in place, is filled to within 1/4 in. of the top with this electrolyte. The cell is then connected and current is allowed to flow through the cell. Changes in voltage are automatically recorded (by a Speedomax, Model G, Voltage Recorder, manufactured by Leeds & Northrup). A sharp drop in voltage indicates penetration of the separator by dendrite. The time necessary to produce the voltage drop is taken as a measure of the separator's ability to resist dendrite penetration. This time depends of course on the current density and the first aim is to find the current density that will result in the shortest, reproducible penetration times for any given material.

This test is expected to show differences in the resistance of individual separator materials to penetration by dendrites. It should also make it possible to evaluate the effects of different treatments on the ability of cellophane to resist dendrite penetration.

The rate at which penetration occurs depends on the current density. At low current densities, the zinc is deposited in a spongy form. This sponge is too soft to penetrate the membrane. In tests at a current density of 3 amp/cm², no penetration was registered in 72 hours. At high current densities, on the other hand, an increasing proportion of the current is consumed in gas evolution, the plating efficiency drops and the growth rate is no longer determined by the current density. Typical results, obtained on cellophane follow.

<u>Current density</u> <u>(ma-cm²)</u>	<u>Time to voltage drop</u> <u>(minutes)</u>
1	No break
2	" "
3	" "
6	150
8	118
10	106
12	114
35	125

The time vs current density curve appears to drop steeply, go through a minimum at about 10 ma/cm², and then rise again gradually. However, the picture is obscured by fluctuations in the voltage due to the growth, breaking off and

resumed growth of dendrites. This method should be capable of differentiating between the dendrite arresting ability of different materials, but it will have to be refined before it can serve this purpose.

Reaction and Diffusion of Silver Ions in Separators

The radioactive tracer study of the reaction of separator material with Ag_2O dissolved in 31% KOH has been completed with the testing of nine separators including six modified cellophanes, inert microporous plastic materials and a modified poly (methacrylic acid) membrane. The test procedures for diffusion and reaction rate measurements have been described in the Fifth Quarterly Progress Report.

Modified Cellophanes

Two samples of PUDO-300 cellophane were treated in solutions of gelatinizing agents to alter the surface pore structure. One sample was soaked 2 hours in 20% ZnCl_2 solution and the other was soaked 1 hour in 20% $\text{Al}_2(\text{SO}_4)_3$ solution. The cellophane treated in ZnCl_2 reacted more slowly with dissolved Ag_2O than untreated cellophane. The half time of the reaction (the time required to reduce the dissolved silver content of the tracer solution to one-half the initial concentration) was 1.2 hour compared to 0.8 hour for untreated PUDO-300 cellophane. The sample treated with $\text{Al}_2(\text{SO}_4)_3$ was extremely brittle when dry and tended to disintegrate after soaking a few hours in 31% KOH. The half time of the reaction with Ag_2O dissolved in 31% KOH was 0.5 hour. This reaction rate was considerably faster than that of any other cellophane tested in this investigation. The results obtained with both these materials are shown in Figure 1 in which the fraction, A/A_0 , of the original Ag_2O concentration remaining untreated after each interval is plotted vs time of contact of the separator sample with the tracer solution.

Reaction rate and diffusion tests were carried out on two samples of silver-treated cellophane (C-19-300 and C-19-600), supplied by NASA-Goddard. As shown in Figure 2, both types reacted with dissolved Ag_2O at nearly identical rates, the half-time being 1.05 hour for both separators. In diffusion tests neither separator permitted diffusion of dissolved Ag_2O at a rate large enough to measure.

PUDO-300 cellophane which had been treated with hydroquinone to increase oxidation resistance reacted with dissolved Ag_2O at a slightly slower rate than untreated cellophane as shown in Figure 3. The half time of the reaction with

hydroquinone (HQ) treated cellophane was 0.95 hour.

Cellophane containing glycerin was treated with tolylene diisocyanate and its rate of reaction with dissolved Ag_2O was measured and compared with that of glycerin-free cellophane which had been treated in the same way. Both materials reacted almost completely with the Ag_2O dissolved in the tracer solution in 6 to 10 hours. As shown in Figure 3, the cellophane which initially contained glycerin (TDI-2) reacted somewhat faster at the beginning of the test (half time 1.15 hour) than did glycerin-free cellophane (TDI-1) (half time 1.9 hour).

PMA Membranes

Previously reported results on the extent of the reaction of dissolved Ag_2O in PMA membranes indicated that these separators had only a limited capability of preventing migration of silver by reacting with silver ions. In order to increase the probability that silver ions would react in the membrane before diffusing through it, a portion of the starch pore-former was deliberately retained in the porous polyethylene base material in which the methacrylic acid-divinyl benzene mixture was subsequently polymerized. The behavior of this modified PMA membrane in contact with Ag_2O dissolved in 31% KOH indicated that the starch reacted slowly with the silver ions and eventually removed most of the silver from solution. After one day in contact with the tracer solution the 0.25 gm separator sample had reacted with 30% of the dissolved Ag_2O and was continuing to react after six days when the solution activity (Ag_2O content) was only 20% of the original value.

Microporous Plastic Separators

Of the two microporous plastic separators which were tested, the porous polyethylene (MIPOR 12 CN) was apparently not inert in the tracer solution. The activity of the solution decreased fairly rapidly during the first 24 hours of the test and then remained nearly constant. The dissolved Ag_2O content of the solution had decreased to 78% of initial after 24 hours but after 42 hours the Ag_2O content was still 75% of the initial value. The presence of residual pore-former (starch) in this separator was probably responsible for the observed uptake of silver ions.

The microporous poly(vinyl chloride) separator (MIPOR 34 CN) was more inert in Ag_2O solutions in 31% KOH. In 48 hours, less than 8% of the Ag_2O originally in solution had reacted with the separator sample.

Summary and Conclusions

1. Ion exchange membranes were made by copolymerizing various monomers with methacrylic acid in a matrix of microporous polyethylene. Their electrical resistance values were satisfactory though it was found that the membranes showing the lowest electrical resistance were least resistant to oxidative degradation. A membrane obtained by copolymerizing isopropyl acrylamide with methacrylic acid stands out in this class and warrants further attention. Its ability to stop Ag_2O diffusion remains to be tested.
2. Other ion exchange membranes were prepared by incorporating ion exchange resins in a polyurethane matrix. Their electrical resistivities are promising; their oxidation resistance is intermediate.
3. The tests on cellophane, treated with antioxidants, were completed with the examination of a hydroquinone treated sample. Electrolyte absorption and retention were slightly reduced, electrical resistivity was slightly decreased, the swelling in electrolyte was reduced by the treatment. The oxidation resistance was greatly improved and the silver reaction rate was somewhat slower than in untreated cellophane. The hydroquinone treatment appears therefore to offer several advantages without serious drawbacks.
4. The samples of silver treated cellophane submitted by NASA showed reduced swelling in electrolyte (except at -26°C), moderate decreases in electrolyte absorption and retention, and virtually no change in electrical resistivity when compared with untreated cellophane. The reaction rate with dissolved Ag_2O was moderately slower than in untreated cellophane. There was no measurable Ag diffusion. Silver treatment appears therefore to be beneficial.
5. Gelatinization of cellophane with zinc chloride slowed the reaction rate with Ag_2O to a moderate extent. The effect of the ZnCl_2 treatment on the growth rate of zinc dendrites remains to be tested.
6. Treatment with alum, as another means to reduce the pore size of cellophane, is unsatisfactory since it results in a serious decrease in the chemical stability of the membrane.
7. Diisocyanate treatment of cellophane results in improved dimensional and chemical stability, and a moderate increase in electrical resistivity,

without any marked effect on the electrolyte adsorption and retention. The reaction rate with Ag_2O is reduced but silver diffusion remains too small to be measured. These results warrant further consideration to be given to this treatment.

8. A method for measuring the ability of separator materials to resist penetration by zinc dendrites is under investigation. When perfected, it should make it possible to assess the effectiveness of separator modifications.

Future Work

1. The evaluation of our ion exchange membranes is to be completed.
2. The diisocyanate treatment of cellulosic materials is to be perfected.
3. The zinc dendrite study will be continued, with a view to improving the resistance of separator materials to penetration by dendrites.
4. We will build silver-zinc plate stacks, incorporating the most promising separator materials, based on the results of our screening tests. The complete assemblies will be housed in containers which will be supplied by NASA. The batteries will be submitted to NASA for evaluation.

Literature Cited

- (1) U. S. Dept. Interior, Office of Saline Water, Research and Development Report No. 69, "Investigation and Preparation of Polymer Films to Improve the Separation of Water and Salts in Saline Water Conversion", by Monsanto Boston Laboratories, Everett, Mass., December 1962 (also available from OTS as PB 181467).
- (2) Thomas W. Higgins, "The Causes and Prevention of Dendritic Growth in Zinc Electrodeposition", Ph.D. (Chem. Eng.) Dissertation, Polytechnic Institute of Brooklyn, 1962 (also available from University Microfilms, Ann Arbor, Mich.).
- (3) T. A. Kryukova, "The Growth of Zinc Dendrites in Some Swelling Polymers", Soviet Electrochemistry (Proc. Fourth Conference on Electrochemistry, Oct, 1956). N. Y., Consultants Bureau, 1961 v. 3, p. 147-151 (In English)

Table IV
Electrolyte Absorption and Retention at 26°C

Sample No.	Material	Dry Weight		Thickness		Volume		Absorption		Retention	
		g	g	cm x 10 ⁻⁴	cm x 10 ⁻⁴	dry	wet	g	g/cc	g	g/cc
1	Celloph. PUDO-300	.0683		25	71	48.4	140	.4074	8.4	.1805	3.7
28	" + Hydroquin.	.0866		30	76	58	147	.4827	8.322	.1787	3.08
29	" + ZnCl ₂	.1173		38	84	73.5	163	.5322	7.241	.1670	2.27
30	C-19-300	.0878		33	79	64	153	.4797	7.507	.2016	3.16
31	C-19-600	.1245		48	109	93	211	.4803	5.170	.2527	2.72
2	Celloph. PUDO-600	.1018		41	102	79.3	190	.392	4.9	.2085	2.6
32	Polyisoprop. acrylamide/PE	.2118		76	127	142	246	1.1857	8.060	.5077	3.45
33	Permion 1000	.1127		76	76	147	147	.4166	2.832	.1141	0.78

Table V
 Electrical Resistance (Ohms) in 31% KOH at 26°C
 after different soaking times

Sample No.	Material	5 min	10 min	20 min	1 hour	24 hour
1	Celloph. PUDO-300	0.054	0.049	0.053	0.053	0.062
28	" + Hydroquin.	0.059	0.060	0.058	0.061	0.063
29	" + ZnCl ₂	0.060	0.060	0.053	0.055	0.058
30	C-19-300	0.068	0.070	0.066	0.068	0.069
31	C-19-600	0.101	0.101	0.096	0.101	0.099
32	PMA - Polyisoprop. acrylamide	0.159	0.139	0.151	0.145	0.122
33	Permion 1000	0.182	0.167	0.167	0.186	0.157

Table VI

Electrical Resistance in 31% KOH at 26°C

Sample No.	Material	R _o	Dry Thickness in x 10 ⁻⁴ cm 10 ⁻⁴	Wet Thickness in x 10 ⁻⁴ cm 10 ⁻⁴	% Change	R _i	ρ	
1	Celloph. PUDO-300	.062	10	25	28	71	.009	8.45
28	" + Hydroquin.	.063	12	30	31	79	.009	7.70
29	" + ZnCl ₂	.058	15	38	31	79	.009	7.07
30	C- 19-300	.069	13	33	31	79	.010	8.30
31	C- 19-600	.099	19	43	44	112	.015	8.50
2	Celloph. PUDO-600	.088	16	41	40	102	.013	8.35
32	PMA + Polyisoprop. acrylamide/PE	.122	30	76	61	155	.018	7.8
33	Permion 1000	.157	20	51	22	56	.024	27.1

Table VII

% Dimensional Changes in 31% KOH at -26°C

Sample No.		70 hours			Length	7 days		
		Length	Width	Thickness		Length	Width	Thickness
1	Cellophane PUDO-300	-5	+10	+300	-5	+10	+10	+300
28	No. 1, treated with hydroquinone	-2	+18	+290	-2	+18	+18	+290
29	No. 1, " " ZnCl ₂	0	+17	+210	-2	+15	+15	+210
30	NASA C-19-300	0	+20	+320	0	+20	+20	+315
31	" C-19-600	0	+25	+265	0	+22	+22	+250
32	Porotheene/MAA/i-PAAm	+18	+35	+100	+18	+35	+35	+100
33	Permion 1000	+8	+9	+50	+8	+8	+8	+25
Sample No.		21 days			Length	28 days		
		Length	Width	Thickness		Length	Width	Thickness
1		-10	+10	+280	-10	+10	+10	+350
28		0	+20	+320	0	+20	+20	+320
29		0	+18	+220	0	+16	+16	+215
30		0	+20	+320	0	+20	+20	+320
31		+2	+25	+245	+2	+25	+25	+245
32		+18	+35	+100	+18	+37	+37	+100
33		+8	+8	+5	+8	+10	+10	+10

Table VIII

% Dimensional Changes in 31% KOH + 26°C

Sample No.	Length	70 hours		Thickness	Length	7 days		Thickness	Length	14 days		Thickness
		Width	Thickness			Width	Thickness			Width	Thickness	
1	-5	+5	+280	-5	+5	+5	+200	+5	+5	+5	+170	
28	0	+8	+150	-5	+8	+8	+165	-5	+8	+8	+165	
29	-2	+6	+140	-2	+6	+6	+140	0	+7	+7	+160	
30	+2	+11	+140	+2	+10	+10	+140	+2	+10	+10	+140	
31	+2	+12	+125	+2	+12	+12	+125	+2	+12	+12	+130	
32	+17	+40	+100	+17	+42	+42	+100	+17	+42	+42	+100	
33	+8	+9	+50	+8	+10	+10	+30	+8	+10	+10	+5	
Sample No.	Length	21 days		Thickness	Length	28 days		Thickness				
		Width	Thickness			Width	Thickness					
28	0	+8	+200	0	*	*	+200	Celloph. + Hydroquinone				
29	-3		+170	-3	*	*	+170	"	+ ZnCl ₂			
30	+2	+10	+155	+2	+10	+10	+155	C-19-300				
31	+2	+12	+155	+2	+12	+12	+155	C-19-600				
32	+16	+43	+100	+16	+43	+43	+100	PMA - Polyisoprop. acrylamide				
33	+9	+10	+5	+8	+9	+9	+20	Permion 1000				

* Tests not completed due to sample deterioration

Table LX

% Dimensional Changes in 31% KOH at +90°C

Sample No.		70 hours			7 days		
		Length	Width	Thickness	Length	Width	Thickness
1	Cellophane PUDO-300	-25	+15	+280	-25	+10	+300
28	No. 1, treated with hydroquinone	-2	+5	+200	-2	+4	+215
29	No. 1, " ZnCl ₂	0	0	+130	0	+0	+130
30	NASA C-19-3	+2	+7	+125	+1	+6	+135
31	" C-19-600	+2	+8	+110	+2	+7	+120
32	Porotheane/MAA/PPAam	0	+20	+100	+2	+17	+67
33	Permion 1000	+7	+11	+50	+6	+9	+10

Sample No.		14 days			21 days			28 days		
		Length	Width	Thickness	Length	Width	Thickness	Length	Width	Thickness
1	-30	+5	+300		-30	+5	+260	*	*	*
28	-2	+2	+200		-2	+2	+220	-2	*	+230
29	0	0	+140		0	0	+140	0	*	+200
30	0	+5	+135		0	+5	+145	0	+5	+180
31	+2	+6	+110		0	+5	+120	0	+3	+130
32	0	+13	+35		-2	+10	+50	2 -2	+11	+50
33	+5	+8	+5		+5	+7	+5	+5	+8	+10

* Test discontinued, due to sample deterioration

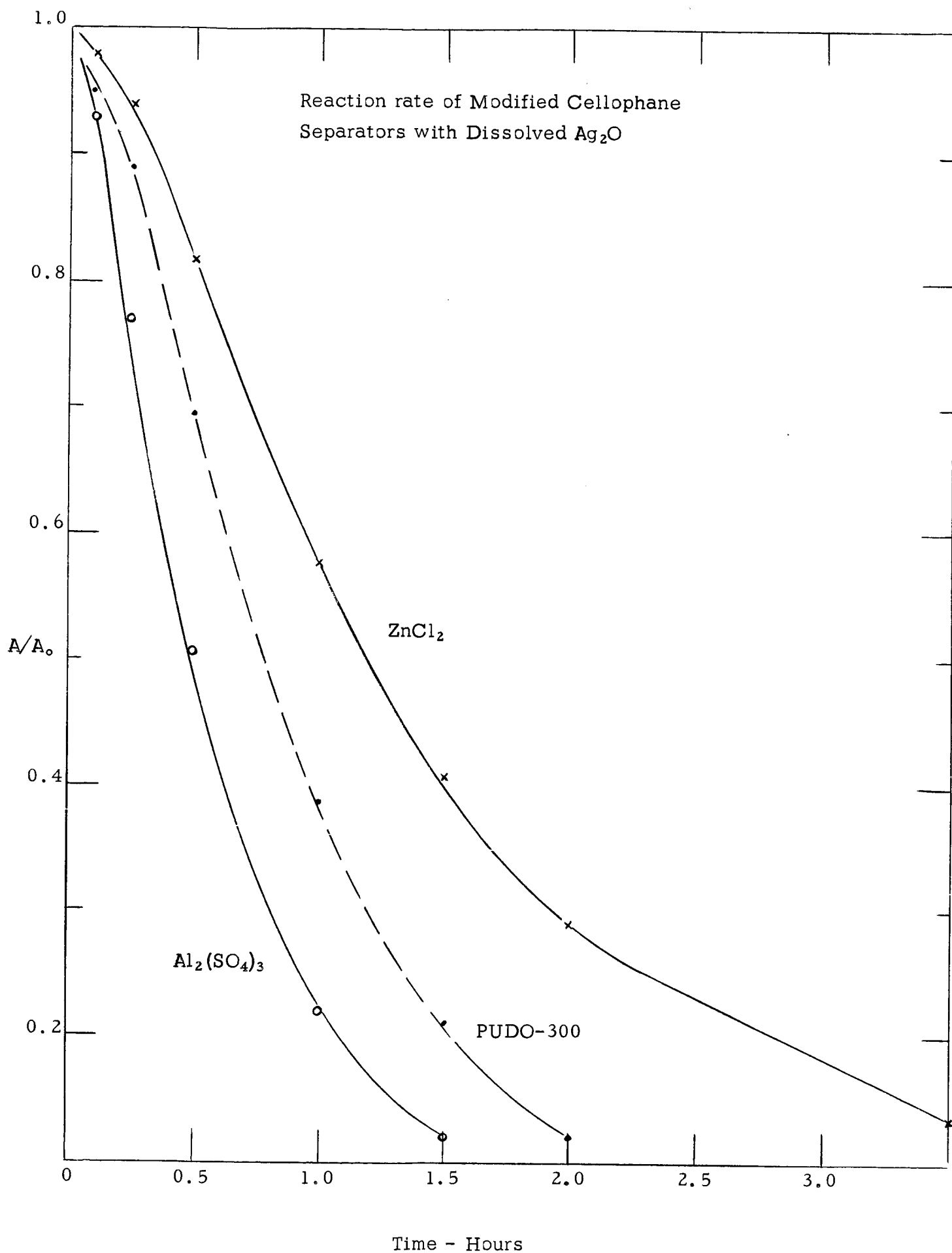


Figure 1

Reaction rate of Silver-treated Cellophane
Separators with Dissolved Ag_2O

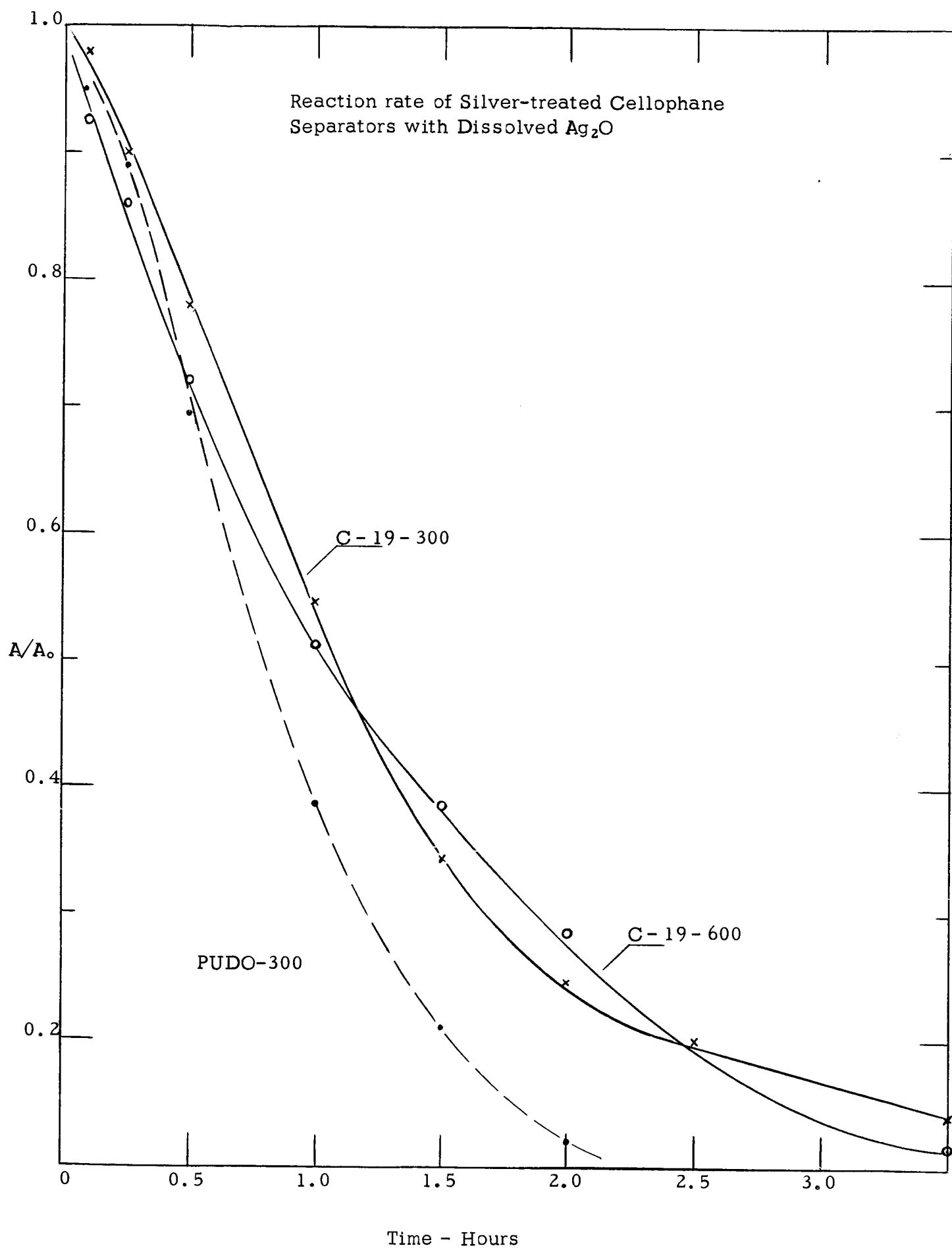


Figure 2

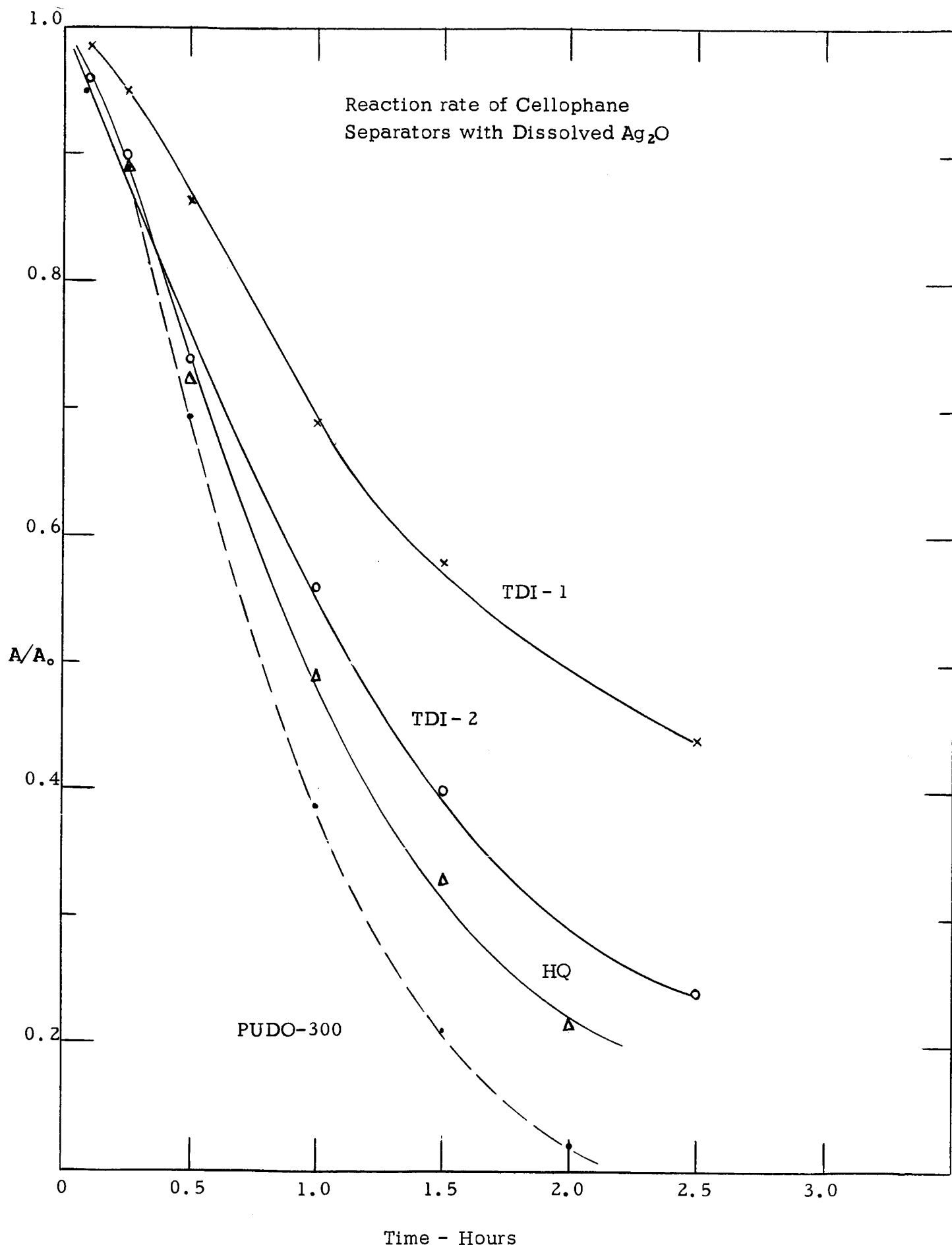


Figure 3

PHOTOGRAPH No. 1

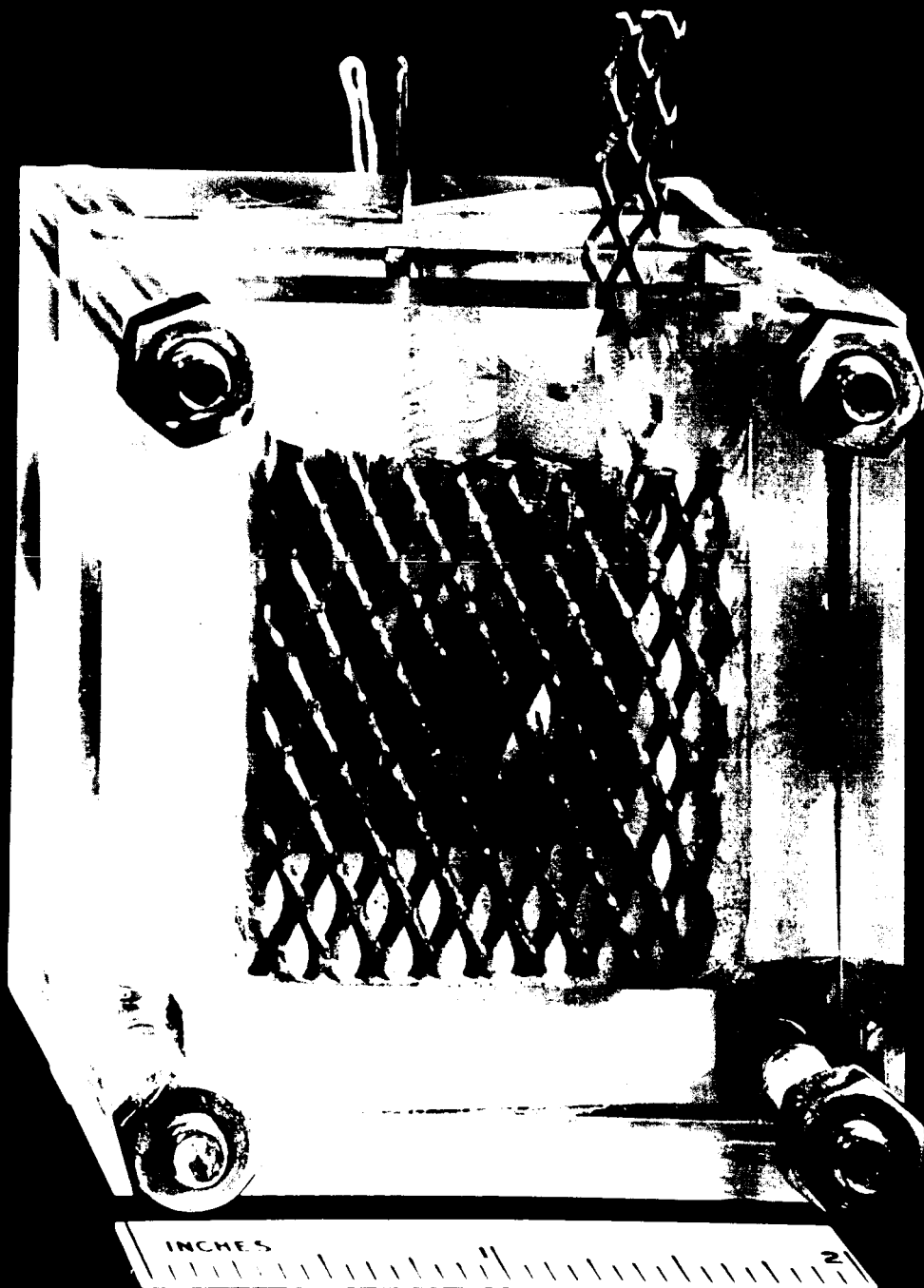
DENDRIT CELL PARTS

PLEXIGLAS
WATER

FRONT CELL WALL
with POSITIVE ELECTRODE

PHOTOGRAPH No. 2

DENDRITE CELL,
viewed from POSITIVE SIDE



NOT REPRODUCIBLE

PHOTOGRAPH No. 3

DENDRITE CELL,
viewed from NEGATIVE SIDE

